

Thermodynamics of Frustrated Quantum Spin Chains

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We apply the transfer matrix DMRG to frustrated quantum spin chains, going down to $T = 0.025$ while being in the thermodynamic limit. The incommensurability problem of exact diagonalization and the negative sign problem of quantum Monte Carlo vanish completely. To illustrate the method, we give results for chains with next-nearest neighbor frustration and the delta chain, which has been a testbed for many thermodynamic methods. By comparison, the DMRG proves to be an extremely powerful method for the old problem of the thermodynamics of frustrated systems.

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In the recent past, there has been enormous interest in one-dimensional quantum systems, concentrating on the Hubbard and Heisenberg models. As analytically exact methods such as the Bethe or the matrix product ansatz can capture only some of the relevant models, particular attention has been paid to the development of numerical methods.

Since one-dimensional strongly correlated systems show strong quantum and thermal fluctuations, the most interesting physics is to be expected close to or at $T = 0$, where only quantum fluctuations survive. To investigate such systems in the low temperature regime, several numerical techniques are used, mainly exact diagonalizations, quantum Monte Carlo, and the DMRG algorithm [1].

In many cases, these methods yield completely satisfying, mutually complementary or supporting results. Some systems, however, have evaded thorough analysis so far. One of the strongest numerical challenges comes from frustrated quantum spin models [2]. These models are both of theoretical and experimental interest, which at the moment concentrates on the famous CuGeO_3 [3].

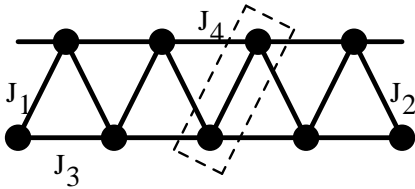


FIG. 1. Hamiltonian studied by the transfer matrix DMRG. The dashed line indicates spins grouped into a new object.

In this letter we show how the transfer matrix DMRG can be applied to frustrated quantum spin systems, such

that thermodynamic quantities can be very reliably obtained down to $T \approx 0.01$ for infinite system sizes, i.e. in the thermodynamic limit. There is no principal restriction of the systems that can be considered. To discuss how this overcomes the difficulties of other methods, we present numerical results for several physically relevant frustrated quantum spin systems.

Let us first recall the other standard techniques. Exact diagonalization techniques either calculate the full spectrum of a very small system or extract information from the low-lying states of somewhat longer systems [4]. In both cases, finite size effects are present, aggravated in frustrated systems by incommensurability effects.

Both the quantum transfer matrix technique [5] and quantum Monte Carlo start from a Trotter decomposition which maps the one-dimensional quantum problem to a two-dimensional classical problem. After a checkerboard decomposition $H = H_1 + H_2$ [6], the partition function is given by

$$Z_m = \text{Tr} [e^{-\beta H_1/m} e^{-\beta H_2/m}]^m, \quad (1)$$

which becomes exact for the Trotter number $m \rightarrow \infty$. In the quantum transfer matrix method, a transfer matrix relating states on sites i and $i + 1$ is written down exactly and thermodynamic quantities are calculated from its maximum eigenvalue. Matrix size grows exponentially with m , restricting to a rather coarse Trotter decomposition, making access to low temperatures difficult; however, results have no finite size effects. Quantum Monte Carlo can access much larger Trotter numbers, while working on finite system sizes. In frustrated spin systems, the essential limiting factor comes from the well-known negative-sign problem: some of the matrix elements of the infinitesimal evolution operator acquire negative signs, but must be interpreted as positive probabilities. Only partial elimination of this problem has been achieved [7–10].

Recently, the application of the DMRG to both classical [11] and quantum [12] transfer matrices has been proposed. For the Heisenberg chain, thermodynamic quantities can be calculated very well [13,14]; in fact, the results are also superior to those obtained from related attempts to apply DMRG techniques to thermodynamics [15]. However, for the systems studied, other methods had already yielded very good results [16].

Here, the transfer matrix DMRG is applied to the more challenging frustrated spin- $\frac{1}{2}$ Hamiltonian

$$\mathcal{H} = \sum_i J_1 \mathbf{S}_{2i} \cdot \mathbf{S}_{2i+1} + J_2 \mathbf{S}_{2i-1} \cdot \mathbf{S}_{2i} + J_3 \mathbf{S}_{2i} \cdot \mathbf{S}_{2i+2} + J_4 \mathbf{S}_{2i-1} \cdot \mathbf{S}_{2i+1} + H S_i^z, \quad (2)$$

as shown in Figure 1. It comprises various frustrated spin models of interest.

The modifications to the original transfer matrix DMRG for an unfrustrated antiferromagnetic chain [13,14] are very simple in principle. First, we rewrite the frustrated spin chain as a spin ladder problem. If we group two neighboring spins- $\frac{1}{2}$ into one object with 4 states, every second nearest neighbor interaction is absorbed; the others and the next-nearest neighbor interactions become effective nearest-neighbor interactions. Similar in spirit to the restructuring method of Munehisa and Munehisa [10] and Nakamura's procedure for alleviating the negative sign problem in quantum Monte Carlo [9], we are now free to choose any basis of the two-spin object which consists of eigenstates of S^z , to maintain the good quantum number [17] of transfer matrix DMRG,

$$\sum_j (-1)^j (S_i^z)^j, \quad (3)$$

where the sum runs along the Trotter direction.

For a $S = 1/2$ problem, these are essentially the Ising basis $|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle$ and the singlet-triplet basis $|\uparrow\uparrow\rangle, (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)/\sqrt{2}, (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2}, |\downarrow\downarrow\rangle$. Numerically, we find that both yield the same results, though the latter has no update of its internal bond in a transfer matrix step and might therefore be expected to be more precise. All results given below were obtained with the singlet-triplet basis.

The transfer matrix DMRG is governed by the parameters M , the number of states kept, and β_0 , the initial temperature and at the same time the stepwidth of the values of β considered during the DMRG iterations. As the two-spin object has 4 instead of 2 states, for given computational resources, M has to be halved. To estimate the effect on DMRG precision (and also check the correctness of the program), we applied both the original and our transfer matrix DMRG to the unfrustrated Heisenberg chain. We find that the new version shows much better results for $M/2$ than the original one for M states kept, as every second bond is taken into account exactly. This greatly enhances the applicability of this method also to frustrated chains. To give one result, the internal energy per site of the isotropic Heisenberg model should go to -0.4431 for $T \rightarrow 0$. For $M = 32$, the original transfer matrix DMRG extrapolates -0.448 for $\beta_0 = 0.2$, ours gives -0.445 for $M = 16$ only.

There are several advantages of the transfer matrix DMRG for frustrated spin systems. As opposed to the exact diagonalisation of small systems, we have no incommensurability problem, as we work in the thermodynamic limit right away. Unlike quantum Monte Carlo,

there is no such thing as a negative sign problem; also quantum MC results are obtained in finite systems, albeit often rather large ones. Compared to the recent progress made by Nakamura [9], DMRG works for *all* frustrated spin systems; furthermore, there is no problem with the susceptibility. Quantum transfer matrix methods are closest in spirit to the transfer matrix DMRG. They relate to each other exactly as $T = 0$ DMRG relates to exact diagonalisation. Like $T = 0$ DMRG that can treat much longer systems than exact diagonalization, here much higher Trotter numbers can be obtained: Typically, in quantum transfer matrix problems one is restricted to less than 10 Trotter slices when dealing with frustrated problems. The transfer matrix DMRG has no fixed number of Trotter slices; it increases with β . Consider $T = 0.025$, or $\beta = 40$ as a typical low temperature one might wish to reach. For a realistic starting temperature $\beta_0 = 0.05$, this implies 800 Trotter slices at that temperature, or 800 DMRG steps. While maintaining the advantages of the quantum transfer matrix, the problem of convergence of results in the Trotter number can be virtually eliminated, as the results presented here show. However, the problem of convergence in the number M of states kept has also to be considered. Working with $M \leq 32$, which is still possible on a workstation, we find that down to $T \approx 0.05$ results are very well converged; for lower T the trend is very clear (see as an example the inset of Figure 4).

In order to test the transfer matrix DMRG, we have first applied it to the so-called delta chain, because it exhibits a rather special low-temperature behavior [20], of which some approximative analytic results are known [21]. Numerical methods [7,8,20] have been applied to this chain with varying success, which makes this a good starting point for a comparison of results.

The delta chain consists of spin triangles, which are linked through the triangle basis spins ($J_1 = J_2 = J_3 = 1$, $J_4 = 0$). It can be understood as a frustrated chain with next-nearest neighbor interactions, of which every second has been taken out. It has the same doubly degenerate ground state as the Majumdar-Ghosh model, with spin singlets sitting either on all left or on all right sides of the triangles [18]. Numerical studies reveal that the delta chain gap $\Delta \approx 0.22$ is much smaller than the Majumdar-Ghosh model [19] gap, which suggests a rather delocalized excitation [20]. On the other hand, exact diagonalisation shows an almost flat dispersion relation, indicating a localized excitation; these results are however strongly size-dependent [20]. It has been suggested that there are two types of excitations in the chain, kinks and antikinks [21,22]. Elementary excitations can be imagined as domain walls between ground state segments with a singlet on the left to singlet on the right or right to left flip. In the former case, it is energetically favorable to insert one triangle with a singlet on the basis. This is low in energy, being an eigenstate of the local triangle Hamiltonian, but

localized. In the latter case, one triangle has no singlet at all, which is high in energy. However, this triangle can be delocalized. Obviously, kink and antikink excitations must alternate. Thus the spectrum finds a natural explanation.

For the specific heat, the presence of two different excitation types with different energies implies a two-peak structure, with a conventional high-temperature peak and an additional low-temperature peak.

We have calculated the specific heat $C_v(T)$ by numerical differentiation of the internal energy which was directly evaluated by the DMRG, starting from temperatures $\beta_0 = 0.5, 0.4, 0.2, 0.1$ and 0.05 , while retaining $M = 16, 24$ and 32 states, down to temperature $\beta = 40$. This implies maximum Trotter numbers $m = 80, 100, 200, 400$ and 800 .

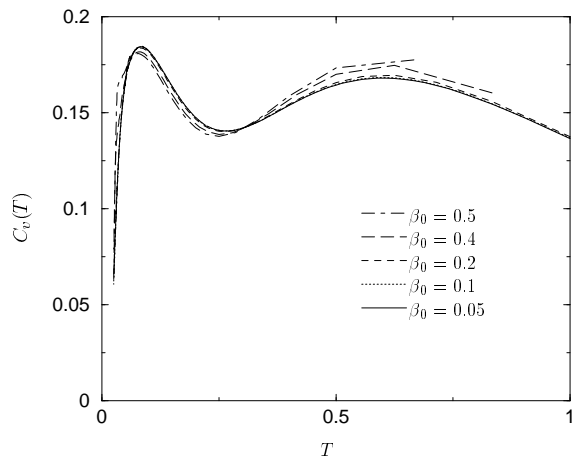


FIG. 2. Specific heat of the delta chain for 32 states kept and various β_0 . Note the different convergence behavior of the high- and the low- T peak.

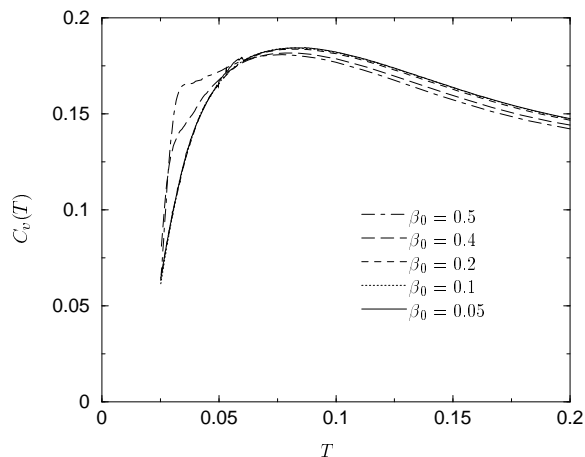


FIG. 3. Low temperature peak of the specific heat of the delta chain ($M = 32$). Curves for $\beta_0 = 0.1$ and 0.05 are almost indistinguishable.

We find that the low-temperature peak in the specific heat is converged both in β_0 and M ; we extract thermodynamic limit values of $T_{peak} = 0.082(2)$ for the peak temperature and a value $C_v^{max} = 0.184(1)$. Calculating the specific heat from a variational ansatz, Nakamura and Kubo [21] predict this second peak at $T \approx 0.05$, with a height of $C_v \approx 0.24$. Numerically, Kubo finds $C_v^{max} \approx 0.18$ at $T_{peak} \approx 0.12$ from a quantum transfer method [20]; these are unextrapolated results from his maximum Trotter number. Otsuka finds $C_v^{max} \approx 0.20$ at $T_{peak} \approx 0.12$ from a recursion method [23]. Monte Carlo studies have reached the high-temperature slope of the low- T peak of C_v , but could not localize and estimate it reliably [8]. The DMRG therefore clearly gives the quantitatively most accurate results; Nakamura's modified Monte Carlo [9] should in principle be capable of a similar precision for the problem under study; it must be stressed that this is because the delta chain fits his negative sign problem elimination formula which is however not universal. The DMRG exploits no special feature of the studied frustrated system and is thus more versatile.

Let us comment on the convergence of the specific heat with $\beta_0 \rightarrow 0$. The underlying internal energy is uniformly underestimated for finite β_0 , converging as β_0^2 . However, as can be seen in Figure 2, for coarse Trotter slicing, the high-temperature peak is overestimated, while the low-temperature peak is underestimated (a similar phenomenon is also visible in Ref. [20]). This can be understood in terms of a “sum rule”. Obviously,

$$s(T = \infty) - s(T = 0) = \int_0^\infty \frac{C_v(T)}{T} dT. \quad (4)$$

Now all the classical models resulting from the Trotter decomposition have vanishing zero-temperature entropy, while they all map free spins for $T \rightarrow \infty$, i.e. $s(T = \infty) = \ln 2$, yielding a constant value of the integral for all β_0 . Thus the errors due to the Trotter decomposition have to compensate each other; a coarse decomposition will miss low- T features and overemphasise high- T features. The shoulders for $\beta = 0.5$ and 0.4 in Fig. 3 we interpret as a low- T cutoff of C_v due to large β_0 .

For a comparison, the specific heat (Fig. 4) of a typical next-nearest neighbor frustrated chain (the spin- $\frac{1}{2}$ chain at its transition point $J_1 = J_2 = 1$, $J_3 = J_4 = 0.2411$) has a one-peak structure, which is converged down to $T \approx 0.04$ and can be linearly extrapolated to $C_v = 0$ at $T = 0$. For very low temperatures, the results deviate towards higher values. We find that both a too coarse Trotter decomposition and a too small M lead to an overestimation of C_v ; comparing the curves for $\beta_0 = 0.1$ and $\beta_0 = 0.05$ indicates that the remaining error is almost entirely due to the finite number M of DMRG states. As the inset in Fig. 4 shows, even for very low T the results converge fast with M .

Let us finish by showing the susceptibility of the delta chain in comparison to the exactly known susceptibility

of the isotropic $S = \frac{1}{2}$ Heisenberg chain (Fig. 5), both calculated by numerical differentiation of the explicitly evaluated magnetisation. Whereas for the latter one finds a finite χ for $T = 0$, here the susceptibility is exponentially activated due to the gap in the excitation spectrum. No particular physics is hidden there, but from the point of view of the transfer matrix DMRG it can be observed that again results converge very fast in β_0 and M .

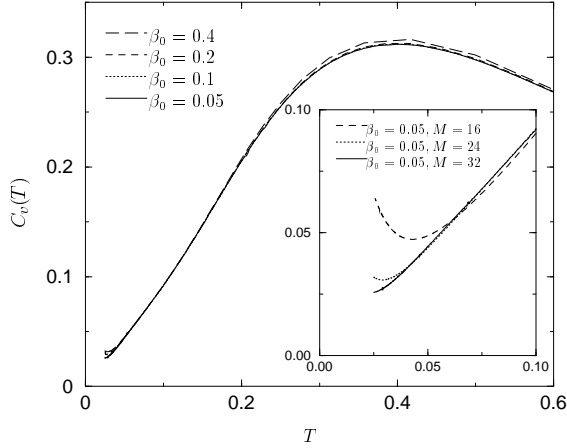


FIG. 4. Specific heat of the next-nearest neighbor frustrated spin- $\frac{1}{2}$ chain at its phase transition ($M = 32$). The inset shows the convergence with the number M of states kept of the $\beta_0 = 0.05$ curve for very low temperatures.

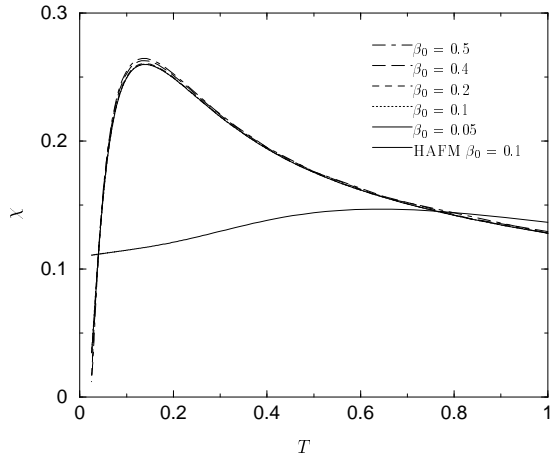


FIG. 5. Susceptibility of the delta chain ($M = 32$) compared to the susceptibility of the Heisenberg chain ($M = 32$).

To conclude, we have demonstrated how the transfer matrix DMRG overcomes the problem of obtaining the low-temperature thermodynamics of frustrated spin chains, while at the same time working in the thermodynamic limit without serious restrictions on the Hamiltonians considered. The method can easily be upgraded to more complicated frustrated chains, where other ad hoc fixtures fail. We are therefore confident that the transfer matrix DMRG will emerge as the most convenient

method for obtaining the thermodynamics of frustrated spin or also frustrated fermionic systems.

All calculations were carried out on a 533 Mhz alpha with Linux and a 16 processor T3E.

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